Non-noble metal Manganese Oxide catalysts for the selective hydrogenation of *α,β*-unsaturated aldehydes and ketones

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Introduction

Selective hydrogenation of *α,β*-unsaturated aldehydes and ketones is of great importance in the production of fine chemical and pharmaceutical industry. Noble metals such as Au, Pt, Re, Ru and Ir are often used as active catalyst sites in chemo-selective hydrogenations. However, considering the expensive cost and limited abundance of noble metals, it is of high interest to develop non-noble metal catalysts for chemo-selective hydrogenations. We have previously shown octahedral manganese oxide with 2x2 tunnel structure (OMS-2) to be a good hydrogenation catalyst and display high selectivity towards hydrogenation of C=C (80% selectivity to hydrocinnamaldehyde at 96% conversion).[1] In contrast to the previous results, herein, we have tuned the hydrogenation of cinnamaldehyde to achieve selective reduction of C=O group, with 95% selectivity to cinnamyl alcohol at 99% conversion using octahedral layered manganese oxide (OL) under basic conditions. Reaction conditions have been optimized, including, choice of catalysts, reaction temperature, solvent system and the addition of additive to the reactor (NaOH, KOH). We have further extended the scope of layered manganese oxides to the hydrogenation of other substrates including ketoisophrone and citral.

Materials and Methods

OMS-2 and OL catalysts were synthesized at QUB, detailed synthesis is described elsewhere.[1,2] Hydrogenations were carried out in a 100 cm^3 Autoclave Engineers autoclave under 10 bar H_2 and at 60-100 °C. In a typical experiment, the reactor was charged with substrate (0.006 mol) and catalyst (0.1 g) suspended in methanol (60 cm^3). The reactor was purged three times then pressurized to 10 bar H_2 and heated to 100 °C and the reaction mixture was agitated at 1500 rpm. The reaction was monitored by sampling at regular time intervals, with analysis by GC.

Results and Discussion

Previously, in the hydrogenation of cinnamaldehyde in 10 mol% methanol in water solvent system, we have shown that the 2x2 tunnel structured OMS-2 catalyst is selective towards the reduction of C=C double bond forming hydrocinnamaldehyde with 80% selectivity at 96% conversion.[1] In this study, we found when the solvent system was changed to methanol from a methanol/water mixture the selectivity changed towards the reduction of C=O bond forming cinnamyl alcohol with 64% selectivity at 69% conversion of cinnamaldehyde. In this case, the reaction rate was found to decrease in comparison to methanol/water solvent system, which could be attributed to decrease in solubility of hydrogen in solution. In the hydrogenation of cinnamaldehyde using layered manganese oxide (OL) as a catalyst, better reaction rates were observed after 5 hours with 80% conversion and 85% selectivity to cinnamyl alcohol. The selectivity to cinnamyl alcohol was further enhanced by addition of NaOH or KOH. In the presence of NaOH, the reaction was complete in less than 4 h with 95% selectivity towards cinnamyl alcohol. In the presence of KOH, the reaction was complete in less than 5 h with 94% selectivity towards cinnamyl alcohol. The hydrogenation of cinnamyl aldehyde was investigated at reaction temperatures of 60-100 °C. There was a linear increase in rate as the temperature increased. The activation energy was calculated to be 39.8 kJ/mol; which indicates that the reaction is free from mass transfer limitations and the hydrogenation occurs under the kinetic regime. Extension of this method to other substrates was successful for example; in the hydrogenation of citral at 80 °C using OL in methanol, 89% conversion was achieved after 6 h, with 85% selectivity to unsaturated alcohols (geraniol and nerol). In the hydrogenation of ketoisophrone at 80 °C using OL as a catalyst in methanol, 95% conversion was achieved after 90 min, with 89% selectivity to levodione, which was similar to the selectivity obtained with OMS-2 as a catalyst.

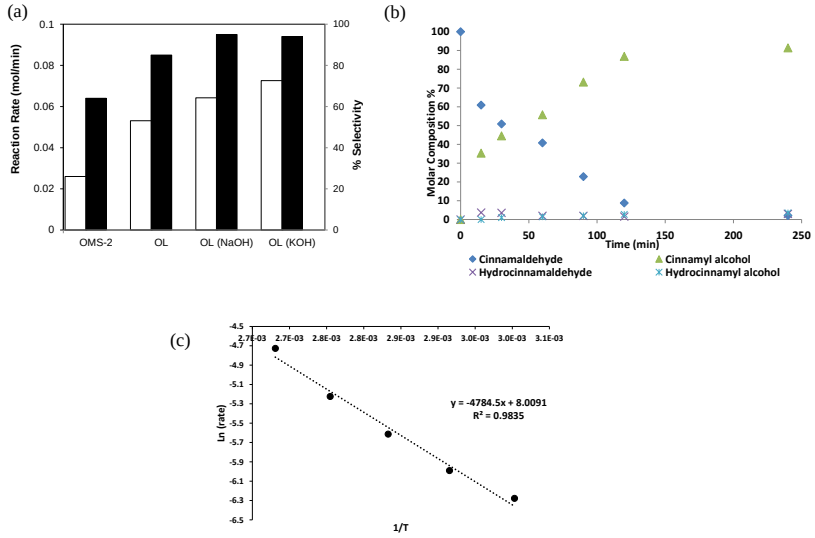

Figure 1 (a) Reaction composition-time profile for hydrogenation of cinnamaldehyde using OL with the addition of NaOH. (b) Comparison of the initial rate of hydrogenation of cinnamaldehyde and selectivity to cinnamyl alcohol using OMS-2, OL, OL (NaOH) and OL (KOH). (c) Arrhenius dependence for the hydrogenation of cinnamaldehyde using OL catalyst.

Significance

OL has been shown to be an efficient and selective hydrogenation catalyst, with selectivity being further enhanced by the addition of NaOH or KOH. OL displays superior activity and selectivity towards hydrogenation of C=O compared to OMS-2. High selectivities and activity was obtained in the absence of noble metals, making this a cost effective method to selectively hydrogenate C=O in high yields.

References

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2. Q. GaO, O. Giraldo, W. Tong, and S. L. Suib, *Chem. Mater*., **2001**, 13, 778.